Nonlinear Optical Properties of Ruthenium Tetraazoporphyrin and Phthalocyanine Derivatives Investigated using Time-Dependent Density Functional Computational Methods

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Introduction:

Nonlinear optical properties of certain compounds are extremely useful in applications such as optical limiters, photodynamic therapy, and 3-D optical data storage. It is proposed that nonlinear optical properties are strongly affected by the structure of a molecule. In this study we used computational methods to investigate structural effects on nonlinear optical properties of metal phthalocyanines.

From experimental studies completed by Jeff Fitzgerald at the U.S. Naval Academy, we know that Ruthenium(II) Tetraazoporphyrin (TAP) is not a nonlinear absorber while Ruthenium(II) Phthalocyanine (PC) shows these properties. The structural difference between the two molecules is the four benzo groups on the PC molecule. For our research we are calculating excitation energies and simulating each molecule's absorption spectrum using Density Functional Theory (DFT). We then systematically add benzo groups to TAP molecular structure and compare the generated spectrum of the new molecule with the simulated spectra of TAP and PC, which allows us to hypothesize whether or not the new molecule would exhibit nonlinear optical properties. Furthermore, we can visualize molecular orbitals and observe how they change as the molecules show nonlinear optical properties.

Background:

In order to understand nonlinear optical properties we must first explore what happens when a photon is absorbed by a molecule.

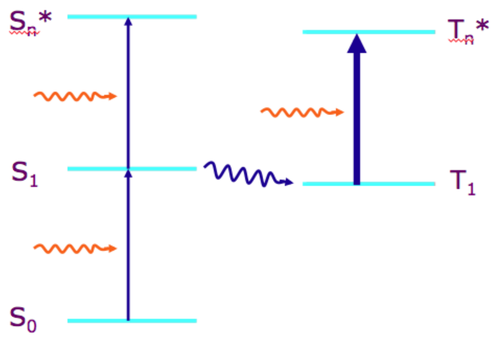


Figure 1: 5 Level Energy Diagram Illustrates what energy states a molecule can occupy when a photon of light absorbed.

When a molecule is in its ground singlet electronic state, we label it S_0. When the molecule is in this state it can absorb a photon of light and become excited to the S_1^*, a vibrationally excited level of the first excited singlet state. At this point the molecule will lose a small amount of energy as heat to reach a more stable vibrational state, S_1. From here two things can happen: Another photon of the same wavelength as before can be absorbed while the molecule is in the S_1 state and excite the molecule to the S_n^* energy state. For metalophthalocyanines this process has a low probability of happening since the excited S_1 is short lived. However, what we expect occurs is that an electron in the S_1 state flips its spin through a process known as intersystem crossing and the system converts to a lower energy triplet state, T_1. From here another photon of light can be absorbed and excite the molecule to the T_n^* state. If the T_1 state has a stronger absorption cross-section than the S_0 state, the molecule will be a nonlinear absorber. This phenomenon is the origin of *sequential two-photon nonlinear absorption*.

Experimental Methods:

These molecules were studied computationally using the program Amsterdam Density Functional (ADF)[1], which is capable of calculating quantum mechanical properties using Density Functional Theory. Every calculation included the same simulated solvent, peripheral methyls, bis-pyridine ligands, and basis set. Our solvent of choice was toluene because of its moderate polarity and it was used for experimental spectra of TAP and PC.

The basis set is the set of functions used to mathematically represent atomic and molecular orbitals. We used STO-QZ4P which is a very large and computationally expensive Slater-type orbital basis set that is comprised of a triple zeta core, quadruple zeta valence, and has four polarization functions. QZ4P was used because it produced spectra that matched experimental data the best.

Next, we choose the correct exchange-correlation functional. For geometry optimizations GGA:BLYP is used. In a geometry optimization the 3-dimensional coordinates of the atoms that make up the molecule are changed until the energy has reached a minimum. For excitation calculations Model:SAOP was used and allows us to calculate each individual excitation energy and its intensity. This information is then used to plot a spectrum of each molecule in the S_0 and T_1 states.

Results:

It turns out that the five level diagram shown in Figure 1 does not completely explain the source of sequential two-photon nonlinear absorption. It turns out that when the molecule is in the S_1 state it can convert to the T_1 state and then relax to the ground triplet state, T_0. From here the molecule can absorb another photon of light and be excited to the T_1^* state.

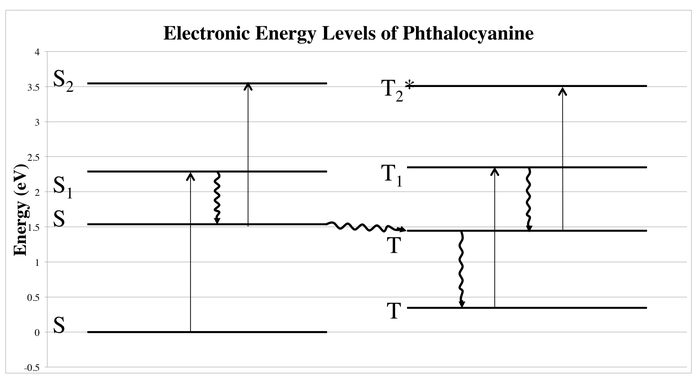
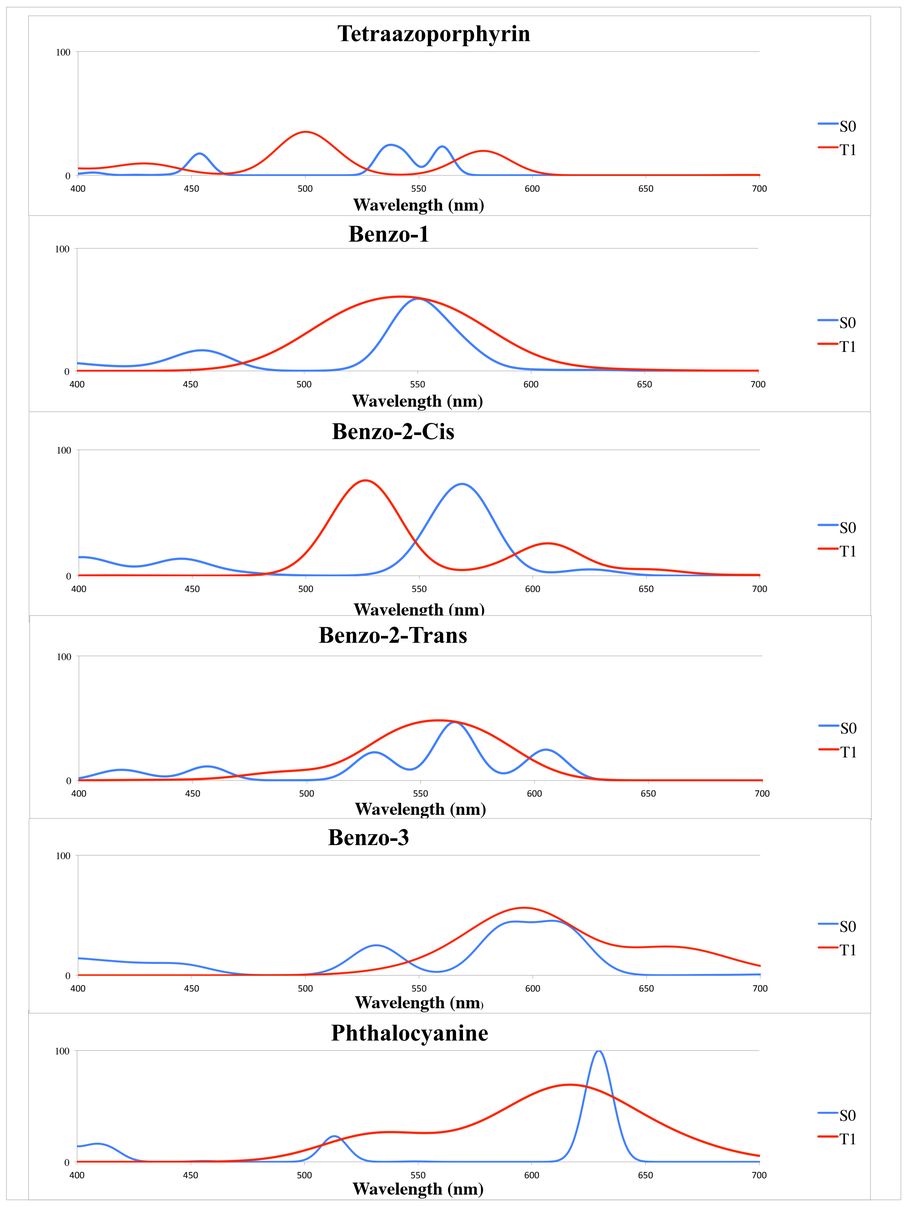


Figure 2: Electronic Energy Levels of PC Using ADF we can determine the electronic energy of each electronic state.



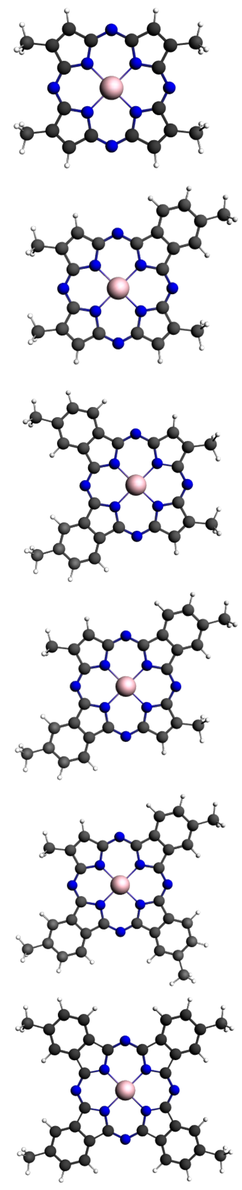
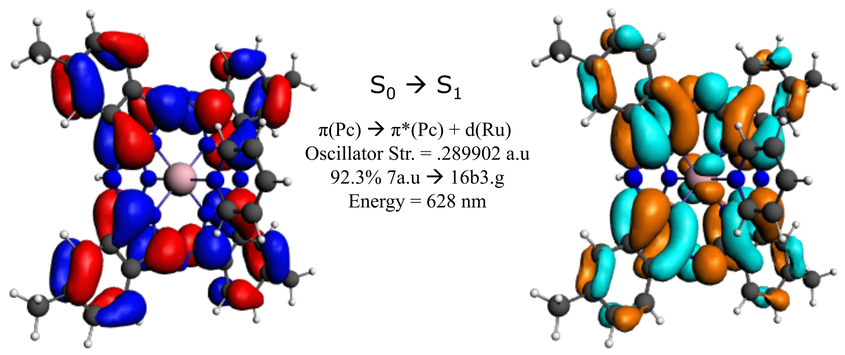


Figure 3: Spectra of Molecules in Question Calculated spectra of the S_0 and T_1 states with intensity normalized to the maximum intensity of Ru(II)PC.

We know that Ru(II)TAP(Py)$_2$ is a linear absorber while Ru(II)PC(Py)$_2$ is a nonlinear absorber which allows us to compare their spectrum to the spectrum of the other four molecules. By doing this we see that the triplet of the PC overlaps the singlet at about 620 nm which hints at nonlinear properties because of the higher intensity of the triplet. This doesn't occur in the TAP spectrum. Using this information we hypothesize that Benzo-1, Benzo-2-Trans, and Benzo-3 will show nonlinear optical properties while Benzo-2-Cis will not since its spectrum is similar to the TAP.

Figure 4: Molecular Orbitals Transitions of PC ADF allows us to visualize the molecular orbitals that contribute to the excitation transitions for each peak in the absorption spectrum. Each color represents a different phase of the orbital and these visualizations will prove vital when we analyze structural effects on the MO transitions.



Future Work:

For the duration of our research we plan on further verifying our calculation methods by reproducing published experimental data of Indium phthalocyanines. Furthermore, Jeff Fitzgerald at the U.S. Naval Academy plans to synthesize the Benzo-1, Benzo-2-Cis, Benzo-2-Trans, Benzo-3 TAP compounds and measuring experimental spectra.

Next, we plan on modifying the molecular structure of these molecules by replacing the benzo groups with electron withdrawing and donating groups in order to investigate the electronic structural effects. We can then analyze the molecular orbital transitions for hints at what structural differences cause these properties.

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References:

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